pH 6.4

Revised by **George F. Ritz and Jim A. Collins**

Illustrations

Tables

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pH is a primary factor governing the chemistry of natural water systems and is measured routinely in U.S. Geological Survey (USGS) studies of water quality. The pH of water directly affects physiological functions of plants and animals and is, therefore, an important indicator of the health of a water system.

> **pH:** A mathematical notation defined as the negative base-ten logarithm of the hydrogen-ion activity, measured in moles per liter of a solution.

The pH of an aqueous system can be understood as an estimation of the activity, or effective concentration,[1] of hydrogen ions (H^+) affecting that system. The theoretical basis of H^+ activity and measurement are described in greater detail in Hem (1989) and in Pankow (1991).

By definition,

$$pH = -log_{10}\,[H^+], \text{ and}$$

$$[H^+] = 10^{-pH}.$$

▶ Logarithmic units are used to express H^+ activity because the concentration of H^+ in most environmental waters is usually too low to be expressed as milligrams per liter, micrograms per liter, or moles per liter, in contrast to most other chemical species (Hem, 1989).

▶ pH is reported on a scale that most commonly is shown to range from 0 to 14 (see TECHNICAL NOTE below). The pH scale is related directly to H^+ and hydroxide (OH^-) concentrations at a given temperature.

— A solution is defined as having a neutral pH (pH = 7.00 at 25°C) when the H^+ concentration is equal to the OH^- concentration.

— A solution is defined as acidic if the H^+ activity (concentration) is greater than that of the OH^- ion (pH is less than 7 at 25°C).

— A solution is defined as basic, or alkaline, when the OH^- concentration is greater than the H^+ concentration (pH is greater than 7 at 25°C).

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[1] The majority of natural freshwater systems for which water-quality data are routinely collected by the USGS are considered to be dilute; that is, the volume of dissolved solids is less than 50 milligrams per liter and the ionic strength of the solution (the strength of the electrostatic field caused by the ions) is less than 10^{-4}. For dilute solutions, activity values can be assumed to be equal to measured ion concentrations (Hem, 1989). Therefore, throughout the text of this section, the terms "activity" and "concentration," as they relate to the hydrogen ion, are used interchangeably.

▶ Temperature affects the chemical equilibria of ionic activities in aqueous solutions, including that of H^+ (Hem, 1989). For example, neutral pH for pure water at 30°C is calculated to be 6.92, whereas at 0°C, neutral pH is 7.48. The pH of pure water at 25°C is defined as 7.00. Therefore, the temperature of the solution must be taken into account when measuring and recording pH.

> **TECHNICAL NOTE:** Although pH commonly is reported on a scale ranging from 0 to 14, pH values of less than 0 can be measured in highly acidic solutions, and pH values greater than 14 can be measured in concentrated base solutions (Nordstrom and Alpers, 1999; Hem, 1989).

6.4.1   EQUIPMENT AND SUPPLIES

The instrument system that is used to measure pH consists of a pH meter, sensor(s) (a pH electrode and often a temperature sensor), and buffer solutions (table 6.4–1). Since a variety of instrument systems are available from manufacturers (multiparameter instruments, for example, are described in NFM 6.8), the procedures described in this section may not be applicable or may need to be modified, depending on the specific instrument system being used. Field personnel should:

▶ Be thoroughly familiar with the information provided in the manufacturer's user manual.

▶ Adhere to USGS protocols for quality control and assurance of pH measurements.

▶ Test the meter and electrode before each field trip.

> **Temperature affects the operation of pH meters, electrodes, and buffer solutions.**

Table 6.4–1. Equipment and supplies used for measuring pH[1]

[mL, milliliters; mV, millivolt; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 degrees Celsius; +, plus: ±, plus or minus; MSDS, Material Safety Data Sheets]

✓ pH meter and pH electrodes
  Battery powered, solid state, with automatic temperature compensation (for multiparameter instruments, see NFM 6.8)
  Range of at least 2 to 12 pH, preferably 0 to 14 pH
  Accuracy of at least ±0.01 units
  Temperature range of at least 0 to +45°C
  Millivolt readout with accuracy of ±1.0 mV

✓ pH electrodes, gel-filled or liquid-filled, as appropriate, for study objectives and site conditions

✓ pH electrode filling solution of appropriate composition and molarity (for liquid-filled electrode)

✓ pH electrode storage solution

✓ Thermistor (or thermometer), calibrated

✓ Buffer solutions for pH 4, 7, and 10; temperature correction chart(s) for buffers; labeled with expiration dates

✓ Stand for holding pH electrode

✓ Bottle, delivery (squeeze), to dispense deionized water

✓ Deionized water, maximum conductivity of 1 µS/cm

✓ Beakers or measurement vessels, polyethylene or Teflon® preferable, assorted volumes of 50 to 150 mL, clean but not acid rinsed

✓ Flowthrough chamber (for ground-water measurements)

✓ Minnow bucket (or mesh bag) with tether or equivalent, used for temperature equilibration of buffer solutions

✓ Waste-disposal container

✓ pH-meter/electrode logbook for recording calibrations, maintenance, and repairs

✓ MSDS for all pH buffers and other reagents to be used

[1]This list pertains to single-parameter instruments for measuring pH. Refer to NFM 6.8 for information on and general use of multiparameter instruments. This list may be modified to meet the specific needs of the field effort.

> **CAUTION: Keep Material Safety Data Sheets (MSDS) readily available and refer to them to ensure that pH buffers or other chemicals are handled safely.**
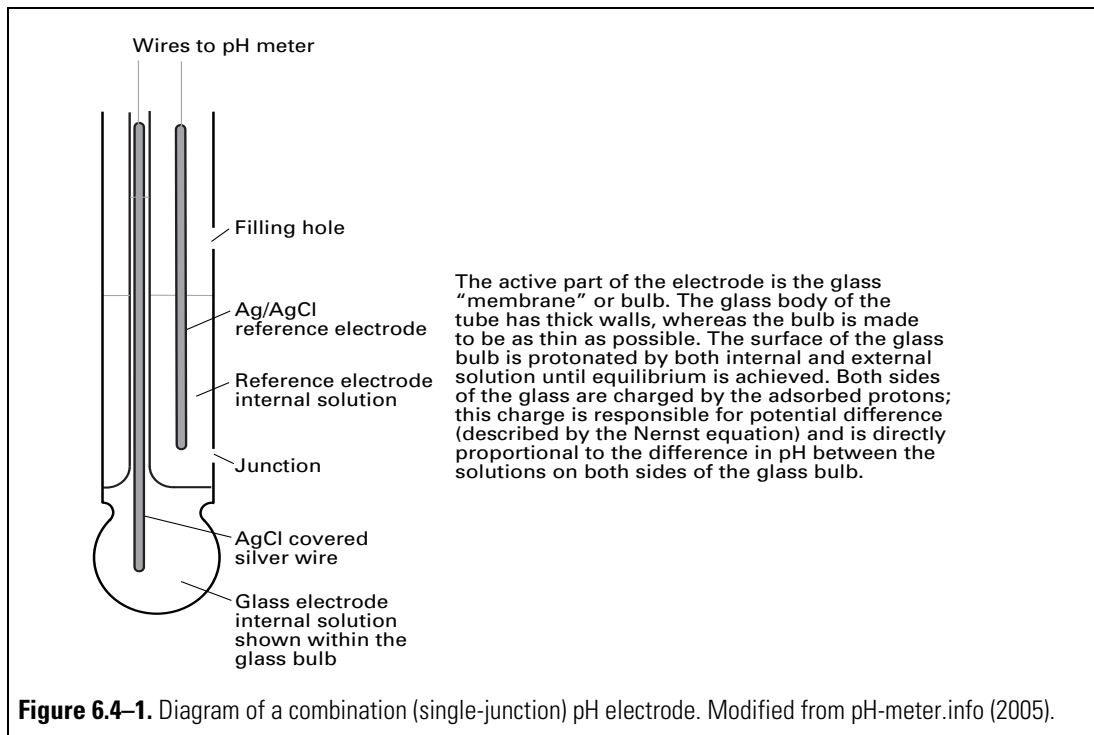
6.4.1.A   pH METERS

A pH meter is a high-impedance voltmeter that measures the very small, direct current potential (in millivolts (mV)) generated between a glass pH electrode and a pH reference electrode. The potentiometric measurement is displayed as a pH value. The meter uses potentiometric differences to generate these pH values and is programmed with (1) the ideal Nernstian response relating hydrogen-ion activity (concentration) and electrical response (59.16 mV/unit pH), and (2) an automatic temperature compensation (ATC) factor. Since the ideal Nernstian slope response from the electrode varies with temperature, the meter's software adjusts the slope to be in accordance with the Nernst equation at the corresponding environmental temperature during calibration and measurement (refer to section 6.4.3 for an explanation of the Nernst equation).

6.4.1.B   pH ELECTRODES

The pH electrode is a special type of ion selective electrode (ISE) that is designed specifically for the measurement of hydrogen-ion concentration in a dilute aqueous solution.

▶ Diodes or triodes (combination electrodes) are used in most USGS field studies.

— Combination electrodes are housed either in a glass or an epoxy body. Diodes contain a pH reference electrode and pH measurement electrode. Triodes contain the reference and measurement electrodes plus a thermistor. In either case, the basic electrode operation is the same (IC Controls, 2005a).

— All combination pH electrodes have a glass membrane, a reference and a measurement electrode, an ionic (filling) solution, and a reference junction (shown on fig. 6.4–1); these are described below.

Wires to pH meter

Filling hole

Ag/AgCl reference electrode

Reference electrode internal solution

Junction

AgCl covered silver wire

Glass electrode internal solution shown within the glass bulb

The active part of the electrode is the glass "membrane" or bulb. The glass body of the tube has thick walls, whereas the bulb is made to be as thin as possible. The surface of the glass bulb is protonated by both internal and external solution until equilibrium is achieved. Both sides of the glass are charged by the adsorbed protons; this charge is responsible for potential difference (described by the Nernst equation) and is directly proportional to the difference in pH between the solutions on both sides of the glass bulb.

Figure 6.4–1. Diagram of a combination (single-junction) pH electrode. Modified from pH-meter.info (2005).

▶ Electrode performance naturally degrades over time with normal use. However, field personnel need to be alert to those chemical environments that can cause serious and more rapid degradation of electrode performance (IC Controls, 2005a). Many such environments are coincident with industrial, mined, and urban areas (table 6.4–2).

— Field personnel should be aware of the effect on the pH measurement when deploying the electrode in such environments: document field conditions on field forms.

— When measuring pH under specific adverse chemical conditions, the use of electrodes with properties designed to withstand such conditions is recommended (table 6.4–2).

Table 6.4–2. pH electrodes recommended for water having elevated concentrations of sodium and other monovalent major cations, sulfide, cyanide, and ferric chloride.

[H^+, hydrogen ion; Na^+, sodium ion; >, greater than; ≥, greater than or equal to]

Chemical condition	Description of water	Degradation effect on a common combination pH electrode	Recommended pH electrode
Basic ions dominant in solution	pH high (>10 pH units); low H^+ activity results in measurement of other monovalent ions in solution.	Sluggish response to changes in pH, resulting from dehydration of the glass membrane.	Glass pH electrode designed for measuring high values of pH.
	Sodium effect: Elevated Na^+ at pH ≥11.0, H^+ activity is low. The electrode senses Na^+ activity as if it were H^+ because of the similar charge and structure of the Na^+ and H^+ ions.	The pH measurement is negatively biased.	Glass pH electrode designed for measuring high values of pH.
Elevated concentrations of sulfide or cyanide	Elevated concentrations of sulfides or cyanides are found in industrial, mined, or urban areas.	Sulfide or cyanide contamination of the internal reference electrode.	Double-junction electrodes and plasticized reference electrodes.
Elevated concentration of ferric chloride	Ferric chloride is used as a flocculating agent in wastewater treatment plants, for example.	Ferric chloride attacks the glass membrane of the pH electrode, deactivating many of the sensing sites on the glass surface.	Consult the manufacturer for (1) selecting pH electrodes that can withstand this environment; and (or) (2) specific cleaning procedures for the glass membrane.

Glass membrane. The most essential and vulnerable element of the pH electrode is the sensitive glass membrane, which permits the sensing of hydrogen-ion activity in most natural waters. When the pH electrode is immersed in a solution (for example, a calibration buffer or a sample solution), ions from the glass diffuse into a thin layer on the outside of the membrane, while hydrogen ions diffuse through this layer until an equilibrium is reached between the internal and external ionic concentrations. In this way, an electrical potential is developed across the sensing surface, which is proportional to the concentration of hydrogen ions in the surrounding solution (pH-meter.info, 2005).

> **A clean, undamaged glass membrane is necessary for performing an accurate measurement of pH.**

Reference and measurement electrodes. Contained within the pH-sensor body are a reference electrode (that generates a constant electrical potential) and a pH-measurement electrode. The measurement electrode generates a separate electrical potential that is proportional to the concentration of hydrogen ions in the sample solution. The electrodes together form a complete electrical circuit; when the diffusion of hydrogen ions reaches equilibrium, no electrical current is present, and the difference in electrical potential that exists between the reference and the measurement electrodes is an indication of the hydrogen-ion concentration in the solution. The pH meter, sensing this minute difference in electrical potentials, converts this difference into a pH value based on the latest calibration of the pH electrode.

Ionic (filling) solutions. An ionic solution used to fill the space within the pH electrode is the source of mobile, chemical ions that serve to complete the electrical circuit between the internal reference and pH-measurement electrodes.The pH electrode may be filled either with an ionic liquid solution (liquid-filled pH electrode) or an ionic gel solution (gel-filled pH electrode). Typically, these ionic solutions contain a chloride salt (usually silver or potassium) of a known and specific molarity (strength). For liquid-filled electrodes, maintaining a sufficient volume and the correct molarity of the filling solution within the electrode is very important to achieving meaningful measurements. Most standard pH electrodes are designed to function well when the electrode filling solution strength is similar to the sample ionic strength, typically having a relatively high ionic strength of 3 molar (M) or greater. Using low ionic-strength or high ionic-strength pH electrodes and a filling solution of appropriate composition and molarity—as recommended by the electrode manufacturer—is recommended when working with environmental samples having conductivities less than 100 μS/cm or greater than 20,000 μS/cm, respectively.

Reference junction. The liquid reference junction (sometimes called the "salt bridge") is an electrically conductive bridge within the pH electrode, between the reference ionic solution and the sample being measured. This junction is necessary for the proper functioning of the pH-sensing electrical cell; it must allow free movement of electrons, but at the same time, isolate the ionic solution from the bulk environmental sample. Typically, this junction is made of a porous material such as ceramic, Teflon, or glass fiber, and may clog and malfunction if not maintained properly. The function of the reference junction is characterized by a chemical memory. In a correctly functioning pH electrode, a small amount of time lapses before the appropriate ionic bridge is formed between the electrode reference ionic solution and the external environmental sample or external calibration-buffer solution. The length of time necessary for the establishment of this ionic equilibrium is a primary reason for the requirement that pH be measured in a quiescent sample solution. (Sections 6.4.4 and 6.4.5 provide further discussion.)

> **Remember to check that the junction on the pH electrode is not clogged; a clogged electrode will not function properly.**

Electrode performance naturally deteriorates over time under normal operating conditions. However, use of the electrode in severe chemical environments can cause more rapid deterioration (table 6.4–2). Many of these environments are coincident with industrial and urban locations: immersing a pH electrode in such environments should be avoided or minimized to the extent possible (IC Controls, 2005a). Whenever the pH electrode is exposed to conditions such as those listed on table 6.4–2, this information should be recorded in the pH-meter/electrode logbook and documented in field notes.

pH BUFFER SOLUTIONS   6.4.1.C

pH buffer solutions (buffers) are ionic solutions that are used to calibrate the pH instrument system. Buffers maintain constant pH values because of their ability to resist changes to the specific pH value for which they are produced. **Measurements of pH are only as accurate as the buffers used to calibrate the electrode.**

▶ Use only buffers that have been certified traceable to an NIST standard reference material.

▶ Select the buffer molarity that is appropriate for the ionic strength of the water to be measured and the instrument system that will be used.

— For pH measurements of dilute waters with conductivities less than 100 μS/cm, use of buffers having lower-than-standard molarity and a low ionic-strength pH electrode is recommended (refer to section 6.4.3.B).

— For pH measurements in high ionic-strength waters with conductivities greater than 20,000 μS/cm, use of buffers having a higher-than-standard molarity is recommended (refer to section 6.4.3.C).

▶ Label pH buffer containers with the acquisition date and the expiration date. Copy the expiration date and the buffer lot number onto any reagent containers into which the buffer is transferred. Copy the temperature-correction information onto the respective buffer container or keep a copy of this information with the buffers being transported to the field.

▶ **Discard the pH buffer on its expiration date**. The pH of a buffer can be altered substantially because of temperature fluctuation, carbon dioxide (CO_2) absorption, mold growth, or evaporation.

Use the following precautions and protocols to help ensure the accuracy of the pH measurement (modified from Busenberg and Plummer, 1987):

• Cap buffer bottles firmly after use to prevent evaporation and contamination from atmospheric CO_2. The pH 10 buffer has the greatest sensitivity to CO_2 contamination, whereas the pH 4 buffer is the least sensitive. Buffers are stable for the short exposure time during electrode calibration.

• Never pour used buffer back into a bottle containing the stock buffer solution.

• Do not insert an electrode or other material into a bottle containing stock buffer solution — **always pour the buffer into a separate container** and discard the solution after use.

• Take care not to contaminate the buffer with another buffer or with other fluids.

• **Do not let the buffer become diluted** (this can happen, for example, if deionized water used to clean the electrode drips into the buffer).

• **Protect buffers against wide temperature variations**, whether in transit, during use, or in storage. Never expose buffers to extreme heat or freezing temperatures. If buffers experience these conditions, their pH values can no longer be assumed to be valid. Discard buffer solutions and any other reagents appropriately.

• Before using buffers in the calibration sequence, bring them to the temperature of the sample solution as much as possible. Since buffer composition differs among manufacturers; check the temperature-correction factors provided by the manufacturer in order to assign the correct pH value to the buffer for the temperature of the buffer at the time of calibration.

> In order of greatest to least sensitivity of standard buffers to CO_2 contamination: pH 10 buffer > pH 7 buffer > pH 4 buffer. In order of greatest to least variation of buffer pH with change in temperature: pH 10 buffer > pH 7 buffer > pH 4 buffer.

6.4.2   MAINTENANCE OF pH INSTRUMENTS

Proper care of pH meters, and particularly of the electrode, is essential for maintaining the accuracy and precision required for pH measurements and promotes the longevity of the equipment. pH instrument maintenance includes adhering to the manufacturer's instructions for the use and care of the instrument, and routine use of appropriate electrode cleaning, reconditioning, and storage requirements. As always, follow the manufacturer's instructions for the specific type of electrode in use.

> Electrode performance must be monitored before every water-quality field trip and again while at the field site.

6.4.2.A   ELECTRODE CARE AND CLEANING

USGS field personnel should integrate the following guidance for the care and cleaning of pH electrodes into their routine field-measurement procedures.

▶ Never handle the glass bulb with fingers. Oily film or scratches on the bulb will interfere with the design characteristics of the glass membrane and affect subsequent pH measurements.

▶ Inspect the electrode and electrode cable for physical damage. For example, check for

— Cut or frayed cable(s).

— Broken connectors and mismatched or missing parts.

— A visibly scratched or broken bulb, cracked electrode body, and broken or damaged internal electrode (reference and measurement electrodes).

▶ Gel-filled electrodes do not require filling and typically require less maintenance than liquid-filled electrodes. Do not store gel-filled electrodes in dilute water, even temporarily, as salts may leach from the gel into the dilute water and produce a large junction potential, resulting in errors in pH measurement.

To prepare and care for liquid-filled electrodes:

1. Remove salt crystal deposits from the electrode, membranes, and junctions by rinsing with deionized water (DIW). Visually check that the reference junction is not blocked or caked with salt. Thorough rinsing with DIW should remove these deposits. Be sure to unplug the fill hole before making pH measurements, as suction pressure may affect the proper movement of ions in the filling solution and the correct operation of the reference junction. Re-plug the fill hole after use.

   • If using an electrode after it has been in a storage solution, uncap the fill hole and suspend the electrode in the air for about 15 minutes. This will allow the filling solution to flush residual storage solution through the porous reference junction and thoroughly wet the junction.

   • After 15 minutes, visually inspect the junction for liquid or new salt accumulation. Ensure that the filling solution is flowing freely. Refer to the manufacturer's instructions.

2. Check the filling solution level and replenish it if necessary. The solution should reach the bottom of the fill hole. **Filling solutions differ in molarity and composition—always check that the correct filling solution required by the manufacturer for a particular electrode is being used.**

3. Drain and flush the reference chamber of refillable electrodes, and routinely refill them with the correct filling solution (check the manufacturer's recommendations).

4. Keep a record of the electrode and meter operation and maintenance and repairs in the pH-meter/electrode logbook.

   • Record in the calibration logbook the operational history of each pH electrode.

   • Record the Nernst slope reading and the millivolt readings at pH 4, 7, 10, or other pertinent pH buffer values (based on field study objectives) during calibration. Properly working electrodes should give 95 to 102 percent response of that expected from the theoretical Nernst relationship (Busenberg and Plummer, 1987).

   > **TECHNICAL NOTE:** The theoretical Nernst response is 59.16 mV/pH unit at 25°C, but varies based on temperature. Adequate adjustment of the Nernstian relation requires manual or automatic temperature compensation (ATC). Most modern pH meters have the ATC feature. A slope of 95 percent or less signals probable electrode deterioration and the need to monitor closely any further decline in slope percent. Consider replacing the electrode if calibration slope values cannot be brought to greater than 95 percent. **Do not use an electrode with a slope of less than 95 percent.**

5. Keep the electrode bulb moist and capped when not in use. Use only the wetting solution recommended by the manufacturer.

For routine cleaning of the pH electrode:

Keeping electrodes clean and the liquid junction free-flowing is necessary for producing accurate pH measurements. Because of the variety of electrodes available, check the manufacturer's instructions for specific tips and precautions.

1. **Before and after each use—**rinse the electrode body thoroughly, using only DIW. Dispense the DIW from a squeeze bottle.

2. Do not wipe or wick moisture from electrodes with paper towels or ChemWipes® as these can scratch the pH glass membrane. Wiping the electrode body with paper also may cause a static charge (polarization) on the exterior of the pH electrode, which can also adversely affect the pH measurement.

6.4.2.B RECONDITIONING OF LIQUID-FILLED ELECTRODES

If problems persist during calibration of a liquid-filled electrode, or if there is reason to doubt that the electrode is in good working condition, check the manufacturer's instructions for how to test and recondition the electrode. Reconditioning procedures should be implemented only if the electrode's slope response has deteriorated to less than 95 percent. Document in the pH-meter/electrode logbook if the electrode has been reconditioned or replaced.

The following general procedures can be used to attempt to bring the liquid-filled electrode back into proper working condition:

1. Remove the old filling solution from the electrode.

    a. Place the needle of a 1- or 3-milliliter (mL) syringe into the electrode filling hole (or use other methods of removing the filling solution, such as vacuum extraction or draining).

    b. Tilt the pH electrode until the filling solution is near the fill hole and the needle tip is covered with the filling solution.

    c. Pull back on the syringe plunger until the syringe is full.

    d. Discharge the solution from the syringe into a waste container and repeat steps 1(a) through (d) until all of the filling solution has been removed from the pH electrode.

2. Flush the pH electrode with DIW.

    a. Use a syringe or squeeze bottle to partially fill the pH electrode chamber with DIW.

    b. With a syringe, remove the DIW from the pH electrode chamber.

    c. As a result of changes in pressure, temperature, and evaporation, visible crystals may form in the pH electrode. If these are present, continue to flush with DIW until all the crystals have been dissolved and removed from the pH electrode.

3. Fill the electrode with fresh filling solution. Flush the electrode chamber with fresh filling solution using a syringe or a plastic squeeze bottle.

    a. Partially fill the pH electrode chamber with the filling solution.

    b. Tilt the pH electrode so that the filling solution will contact all of the internal electrode surfaces.

    c. Remove and discard the filling solution to a waste container.

    d. Refill the electrode chamber with fresh filling solution until the filling-solution level is just below the fill hole. **Be sure to use the appropriate type and molarity of filling solution.**

    e. Rinse any excess filling solution from the outside of the electrode with DIW.

4. After following the reconditioning procedures, retest the electrode. **If the procedures fail to remedy the problem, discard the electrode.**

ELECTRODE STORAGE   6.4.2.C

Electrodes must be clean before they are stored for any length of time. Refer to the manufacturer's instructions for the proper short-term (used daily or weekly) and long-term (2 to 4 months) storage requirements of the electrode.

General guidelines for short-term storage:

1. Storage solutions are specific to the type of electrode; check the manufacturer's manual for each electrode. **Do not store glass hydrogen-ion electrodes in DIW** unless instructed to do so by the manufacturer.

2. Storage solutions have a limited shelf life. Label storage solution containers with the expiration date and discard expired solutions on that date and in a proper manner.

3. Do not place a small piece of cotton or paper towel in the electrode cap to help keep it moist, as this can scratch the glass membrane sensor.

4. Store liquid-filled pH electrodes upright.

5. Store liquid-filled electrodes wet between uses to maximize their accuracy and response time.

   • The glass membrane (bulb) should be fully immersed in the proper electrode storage solution.
   • Between field sites, replace the plug on the fill hole and cover the electrode bulb with the cap.
   • Fill the cap with enough storage solution to keep the bulb wet.

6. Gel-filled electrodes should be stored according to the manufacturer's instructions.

General guidelines for long-term storage:

1. Liquid-filled electrodes may need to be drained of filling solution; follow the manufacturer's instructions.

2. Clean the electrode contacts and connector (with alcohol, if necessary). Allow the contacts to dry and seal and store them in a plastic bag.

3. Store every component of the pH measuring system in an area that is clean, dry, and protected from extremely hot or cold temperatures.

6.4.3   CALIBRATION OF THE pH INSTRUMENT SYSTEM

Proper calibration of the pH instrument system is crucial to accurate pH measurement of environmental samples. During calibration, the pH electrodes are immersed in buffer solutions of known pH (section 6.4.1.C). The buffers are designed to produce a corresponding electrical response potential (usually in millivolts) for the specific pH buffer (for example, pH = 4, 7, or 10 buffer solution) within the pH electrode. These potentials are measured by the pH meter. The Nernst equation gives the expected (theoretical) response potential of the pH buffer at the specific temperature of the calibration (Hem, 1989; see TECHNICAL NOTE below). Note that the measured temperature must be programmed into the pH meter unless the meter has incorporated automatic temperature compensation. The calibration returns the actual, measured potential.

> **TECHNICAL NOTE:** pH electrodes operate on the principle that differing concentrations of the H^+, in buffers or environmental samples, produce differing potentiometric responses (measured in millivolts). The Nernst equation is used to establish the calibration of the pH instrument system by determining the slope of electrical potential versus pH at a given temperature. At 25^{0}C, this Nernstian relation (the slope along any two points on the line plotted for electrical potential versus pH) is known to be 59.16 mV/pH units. To calculate the slope between two points along the line of measured potentials versus pH:

$$E = E^0 - S(pH)$$

where

S = slope

E = electrode pair potential, in mV, and

E^0 = standard potential, in mV.

Thus, using two buffers of known pH (pH_1 and pH_2),

$$E_1 = E^0 - S(pH_1) \quad and \quad E_2 = E^0 - S(pH_2).$$

Rearrange as:

$$s = \frac{E_2 - E_1}{pH_1 - pH_2}$$

The theoretical slope is temperature dependent; the theoretical slope (in mV) can be calculated as:

$$S_t = 0.19841(273.15 + t)$$

where

t = temperature in degrees Celsius, and

S_t = slope at a given temperature.

The primary concept in accurate calibration of the pH electrode is to select pH buffers with values that bracket the expected pH of the environmental sample; this is known as a two-point calibration. Before field calibration of the pH instrument system, it is useful to estimate (or to anticipate from historical site data, if available) the pH and conductivity of the waters to be encountered at the field sites. If no data are available from which to estimate sample pH, then pH indicator paper can be used onsite as a gross indicator of the pH of the system. (**Under no circumstances should a pH value from indicator paper be recorded as site pH.**) For three-point or other multipoint calibrations, follow the manufacturer's instructions for (a) which buffers to use and (b) the sequence of buffer use.

> **EXAMPLE:** When measuring pH in a stream that is within the normal range of specific electrical conductivity,
>
> a. If pH values are expected to be between 7 and 8, then the standard pH 7 and pH 10 buffers should be selected.
>
> b. If pH values are expected to be less than 7, then the standard pH 7 and pH 4 buffers should be selected.
>
> c. If the anticipated pH range in pH is large, a check of electrode performance using a third standard buffer value is advisable.

The following guidelines and standard procedures apply in general whenever a pH instrument system is to be calibrated. Because calibration and operating procedures can differ with differing instrument systems, check the manufacturer's recommended calibration procedures and calibration solutions. Digital pH meters automatically compensate for buffer temperatures and indicate appropriate Nernst values (in millivolts). When using these instruments, follow the manufacturer's calibration instructions precisely—**do not take shortcuts**.

▶ Before each field trip and field calibration, check pH meter/electrode logbook records for electrode performance. **Remember—**any noted calibration slope of 95 percent or less indicates probable electrode deterioration; at 94-percent slope or less, the electrode should not be used.

▶ Use at least two pH buffer solutions of documented, traceable pH value for adequate calibration of the pH instrument system.

▶ Pour the amount needed of each buffer from the source container into a clean, polyethylene bottle dedicated for the respective buffer, and label the bottle with the buffer's pH value, lot number, expiration date, and the temperature-adjusted pH values provided by the manufacturer for that buffer.

▶ The temperature of the buffer solutions should be near the same temperature as the water to be sampled. A calibration check of the temperature sensor must be performed at least annually (NFM 6.1).

> **TECHNICAL NOTE:** Temperature has two effects on the pH measurement of a sample—temperature can affect meter and electrode potentials (Nernstian slope effect), and it can change hydrogen-ion activity (chemical effect) within the sample. The electrode-potential problem can be solved by using an automatic or manual temperature compensator. The change in hydrogen-ion activity resulting from temperature changes in the sample will be minimized if the electrodes, buffers, and container are allowed to equilibrate to the same temperature.

> **Do not use pH buffers that have exceeded their date of expiration.**

6.4.3.A CALIBRATION PROCEDURE UNDER STANDARD AQUEOUS CONDITIONS

"Standard aqueous conditions" refers to environmental water with an ionic strength that is within the range in which a standard buffer solution and combination pH electrode can be appropriately used to achieve an accurate pH measurement. For routine USGS water-quality measurements, ionic strengths ranging from 100 to 20,000 μS/cm are considered standard.

When calibrating the pH electrode:

1. Bring the pH buffers to the ambient temperature of the stream or ground water to be measured, to the degree possible under the prevailing field conditions. The temperature sensor (liquid-in-glass or thermistor thermometer), measurement vessel, and electrode also should be at or near the ambient temperature of the environmental sample. **Maintain each buffer as close to sample temperature as possible when calibrating the electrode.**

   • Surface water and ground water—When equilibrating the buffer temperature to ambient surface-water temperature, one method is to place the buffer bottles in a minnow bucket or mesh bag and suspend them in the body of surface water. Alternatively, place the buffers into a bucket or insulated cooler (a) containing surface water, or (b) being filled with ground water.

   • **When immersing buffer bottles in water, ensure that the bottle is firmly capped and that the water level remains below the cap so that water cannot enter the bottle and contaminate the buffer**.

2. Inspect the pH electrode.

   a. Check for damage to the electrode bulb, body, or cables.

   b. Rinse any mineral precipitate off the electrode with DIW.

   c. Uncover (unplug) the fill hole.

   d. If you can visually see small bubbles within the electrode solution, **gently** tap the electrode body to dislodge them. Bubbles trapped in the sensing tip of the electrode will affect the physical conditions necessary for correct operation of the electrode. **Do not wipe moisture from the electrode.**

3. Power up the pH meter. The meter will perform an internal self-test. Note any discrepancies displayed by the meter and record these in the pH-meter/electrode logbook. Malfunctioning meters usually require manufacturer attention; do not try to fix malfunctioning meters in the field. Having backup meters for field trips is necessary for this reason.

4. Record in the ph-meter/instrument logbook the internal self-test information displayed by the pH meter. A calibration log is **mandatory** for all calibrations.

5. Initiate the calibration process by pushing the required calibration display sequences for the particular pH meter and electrode. **Standard USGS procedure for calibration of a single-parameter pH meter-and-electrode system requires a two- or three-point calibration.**

   • Some types of pH-instrument systems may use a different multipoint calibration procedure; in such cases, follow the instructions provided in the instrument manual.

   • A single-point calibration, recommended by some manufacturers, is not acceptable for USGS field measurement of pH.

6. Record in the pH-meter/electrode logbook: pH value, measured temperature, lot number, and expiration date of the first buffer. Typically, the meter will initially indicate the pH 7 buffer (isoelectric point).

7. Begin calibration procedures:

   a. Note that the electrode and thermistor must be rinsed with DIW at least three times between uses of each buffer.

   b. Rinse the electrode twice with the first buffer (usually the pH 7 buffer). Do not allow the glass membrane of the electrode to come in contact with the sides or bottom of the beaker or other measurement vessel.

      i. **First rinse**—Pour enough buffer into a small beaker or other vessel so that it covers the electrode reference junction; swirl the buffer to rinse the electrode body from above the reference junction to the bottom of the bulb. Discard buffer appropriately.

      ii. **Second rinse**—Pour the next aliquot of buffer into the vessel and immerse the electrode in the buffer for 1 minute. Discard buffer appropriately.

   c. Pour another aliquot of buffer into the vessel. Immerse the electrode for 1 minute, without swirling the buffer solution.

   d. Record the pH measurement shown on the meter display in the pH meter/electrode logbook, along with the buffer temperature reading and the pH value from the buffer and temperature table.

      • For pH meters displaying millivolt values, the meter will display the value associated with the pH 7 buffer, as compensated for the buffer temperature.

      • **For properly functioning electrodes, the pH 7 millivolt value should be between +10 and -10 mV. Record the millivolt data in the pH-meter/electrode logbook.**

   e. Press "Cal" or other display instructions to lock in the pH 7 calibration.

> **TECHNICAL NOTE:** During the calibration sequence, after the DIW and buffer rinses and when the specific buffer value is ready to be locked in to the calibration, some meters provide the opportunity to adjust the initially displayed pH value to a corrected pH value for that buffer solution.
>
>   • **If this adjustment is equal to or less than 0.05 pH units**, proceed with the adjustment, but specifically note this in the pH meter/electrode logbook.
>
>   • **If the adjustment would exceed 0.05 pH units**, the pH electrode is not functioning optimally; consider reconditioning the electrode or using another electrode until the cause of the substandard performance can be determined.

8. **Return to step 6 above, followed by step 7**, repeating each of the procedures just followed but using either the pH 4 or pH 10 buffer, whichever buffer solution, along with the pH 7 buffer, brackets the pH values of the environmental water to be sampled. Record all the calibration data, including the millivolt data, in the pH meter/electrode logbook (see step 7 to test the adequacy of the calibration using the slope test or millivolt test).

9. **At this point, the electrode should be calibrated**. Check the adequacy of the calibration and that the electrode is functioning properly, using the slope test or (and) the millivolt test. Some instruments have the capability to display the slope value; this datum should be recorded in the pH-meter/electrode logbook.

   - **The slope test.** Values ranging from 95 to 102 percent slope are acceptable—if the slope-percent value is outside of this range: clean the electrode and check the level of the filling solution, that the fill hole is open, and that the junction is free-flowing; then, recalibrate.

     > **TECHNICAL NOTE:** Since the theoretical Nernstian relation between electrical response and pH at the calibration temperature is programmed into the pH meter software, the calibration process provides the Nernstian response from the electrode/meter system being calibrated. The actual calibration slope is calculated and the **displayed slope value** represents the actual slope of the electrical potential (millivolt)– pH line that this calibration has produced.

   - **The millivolt test.** For pH meters that display and store only millivolt readings (do not display the slope percent), use the following guidelines to ascertain adequate calibration:

     — pH 7 buffer: Displays between -10 to +10 mV

     — pH 4 buffer: Displays between +165 to +195 mV

     — pH 10 buffer: Displays between -165 to -195 mV

   - If using buffers other than the standard pH 4, 7, and 10 buffers, refer to the information provided with the specific buffer lot to determine the correct, temperature-compensated millivolt potential for that buffer.

10. **Replace the electrode** if, after recalibration, the slope remains outside the acceptable range of 95 to 102 percent or if the acceptable range of the millivolt response is not met at any of the calibration points.

CALIBRATION FOR LOW IONIC-STRENGTH WATER   6.4.3.B

Calibration of pH instrument systems with standard buffers does not guarantee accurate and (or) timely pH measurement in low ionic-strength waters (conductivity less than 100 μS/cm) and in very low ionic-strength waters (conductivity less than 50 μS/cm). As sample ionic strength decreases, the efficiency of the standard pH instrument system also decreases. Low or very low ionic-strength waters have little buffering capacity and may readily absorb atmospheric CO_2, resulting in the formation of carbonic acid in the sample. A continuous change in pH values can occur from the varying reaction rates of the sample water with CO_2, resulting in an unstable measurement.

Standard pH electrodes do not respond well in waters with low ionic strength.

▶ Standard combination pH electrodes respond more slowly, the response is characterized by continual drift, and calibration is difficult to maintain. Equilibration with the sample water may not be completely achieved or the equilibration time may be on the order of hours.

▶ Standard pH electrodes exhibit a jumpy response and are more sensitive to conditions of flow and agitation, and measurement accuracy decreases (Wood, 1981).

When preparing to measure pH in low ionic-strength waters, the response time, accuracy, and reproducibility of the measurement can be improved by modifying the type of electrode and buffer.

To measure pH in water of low ionic strength:

1. Use a specific, low ionic-strength electrode. The pH electrode for low ionic-strength solutions typically is characterized by

   • A thin, responsive glass membrane;

   • A reference junction that allows rapid electrolyte flow; and

   • A pH-neutral ionic additive within the reference filling solution.

2. Use corresponding low ionic-strength pH buffers.

   • The low ionic-strength buffer should contain the same type of pH-neutral ionic additive as that in the electrode reference filling solution (the amount of pH neutral ionic additive must be the same in the electrode and buffer, so that the net pH effect is standardized).

   • Low ionic-strength buffers may not be of the standard pH buffer values (pH = 4, 7, 10). Check that your pH meter can accept these "nonstandard" buffer values for calibration.

> **Calibration of the pH instrument system and measurements made in low ionic-strength solutions should involve a specific combination of low ionic-strength buffers and low ionic-strength electrodes.**

6.4.3.C CALIBRATION FOR HIGH IONIC-STRENGTH WATER

USGS studies increasingly involve pH measurement and sampling of high ionic-strength waters (ionic strength greater than 3 *M* or conductivity greater than 20,000 µS/cm) from sources such as industrial effluent (for example, from paper mills, oil refineries, carbonate processing or other mining activities that have corrosive properties), combined sewer/storm water from urban systems, seawater, and brines. Using standard buffers or standard equipment may not yield an accurate pH measurement for such waters.

▶ The high ionic strength of some industrial effluents or brines often are of greater or equal ionic strength than that of the filling solution in the standard pH electrode. This results in an ionic gradient toward the reference junction and into the pH electrode, which compromises the design parameters of the electrode and therefore the soundness of the calibration and the pH measurement.

▶ Standard buffers are not of an ionic strength that approximates or exceeds the ionic strength of the sample solution, and standard filling solutions in pH electrodes similarly may have too low of an ionic strength to be calibrated properly for measurement of pH in high ionic-strength waters.

When selecting the measurement system to be used to determine the pH of high ionic-strength waters, consider the following options:

1. Obtain high ionic-strength (conductivity greater than 20,000 µS/cm) pH buffer solutions from commercial sources, if available. Follow the guidelines for maintenance and use of pH buffers previously described in section 6.4.1.C, paying close attention to the effect of temperature on buffer values.

2. Obtain high ionic-strength pH glass electrodes, if available. These may be characterized by filling solutions of greater than 3 *M* ionic strength and more solution-specific glass sensors. Note specific uses recommended by the manufacturer and follow the manufacturer's instructions.

3. If no suitable pH glass electrode/buffer system is available for pH measurement in high ionic-strength environments, investigate the suitability of alternative instrumentation and methods, such as those that employ spectrophotometric or optical methods, with respect to the site-specific conditions to be encountered and study data-quality objectives (Bellerby and others, 1995; Farquharson and others, 1992; Sedjil and Lu, 1998).

   • Spectrophotometric methods typically involve the constant-rate introduction of acid-base indicator dyes into the sample; pH measurement is accomplished by measurement of the resultant spectra of the dye. An important limitation to this system is that acid-base indicator dyes are typically sensitive over very narrow pH ranges (Raghuraman and others, 2006).

   • Spectrophotometric measurement of pH in environmental samples is a methodology designed for specific environments; follow the guidelines provided by the equipment manufacturer.

   • As part of USGS studies, any pH data obtained by spectrophotometry or other nontraditional pH measurement method must be entered under the unique parameter and (or) method code designated in the USGS National Water Information System (NWIS) water-quality database.

CALIBRATION FOR THE pH SENSOR IN   6.4.3.D
MULTIPARAMETER INSTRUMENTS

Before beginning calibration of the pH electrode in a multiparameter instrument sonde, read and follow carefully the instrument manual and manufacturer's instructions. Guidelines that incorporate USGS protocols for pH calibration and measurement are described in NFM 6.8.

General procedures for calibration of the pH sensor in a multiparameter sonde:

1. Select the pH 7 and one additional buffer solution that will bracket the anticipated pH of the sample. Equilibrate the temperature of the buffers to the temperature of the environmental sample.

2. Rinse the sonde and electrode thoroughly three times with DIW before and between use of each buffer solution.

3. Rinse the pH and temperature sensors three times with separate aliquots of the first pH buffer, using the "pour-swirl-discard, pour-sit-discard, pour-sit-measure" method described in section 6.4.3.A. Allow enough time for the sensors to equilibrate to buffer temperature before locking in the first calibration point.

4. Repeat step 3, using the second pH buffer, and lock in the second calibration point. (Depending on site conditions and study objectives, it might be useful to check the calibration range of the pH sensor using a third buffer; if appropriate, lock in a value.)

5. Always record temperature information with calibration information in the pH-meter/electrode logbook and on the field sheet.

MEASUREMENT   6.4.4

The pH of sample water is to be measured as soon as possible after removal of the sample from its environmental source. The pH of a water sample can change substantially within hours or even minutes after sample collection as a result of temperature change; degassing (loss of sample oxygen, carbon dioxide, hydrogen sulfide, ammonia); in-gassing (gain of sample oxygen, carbon dioxide, hydrogen sulfide, ammonia); mineral precipitation (formation of calcium carbonate, iron hydroxides); metabolic respiration by microorganisms; and other chemical, physical, and biological reactions (Hem, 1989). Field conditions, including rain, wind, cold, dust, direct sunlight, and direct exposure to vehicle exhaust can cause measurement problems.[2] Always protect the instrument system and the measurement process from the effects of harsh weather and transportation damage.

The pH value of an aqueous system should be determined by taking the median of three or more separate and stable measurements that are recorded in a quiescent sample. Recording a median value ensures that the reported pH value represents a true measurement, instead of a computed measurement, and avoids the mathematical procedure required to compute a mean pH from logarithmic operations.

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[2]The effects of field conditions on the quality of field measurements, water-quality samples, and data integrity must be anticipated by field personnel and protocols to minimize sample contamination as described in NFM 4 and 5 are to be implemented as standard operating procedure.

TECHNICAL NOTE: The pH value of a given sample always is recorded in the USGS database as a median of a series of stable measurements. For applications that require reporting pH over time (for example, an annual average pH) or space, however, computation of the mean of the hydrogen ion activity may be useful. To compute a series of pH measurements collected over time or space:

    a. Take the antilog of each pH measurement, using the following equation: Activity $= 10^{-pH}$.

    b. Add all the antilog values and divide the sum by the total number of values.

    c. Convert the calculated mean activity back to pH units, using the equation, pH = (-log10) (mean H^+ activity).

If reporting pH as a computed mean, document this information and the procedure used. **Do not enter a mean pH value in the USGS NWIS database under the parameter code for a median or direct determination of pH.**

6.4.4.A   pH MEASUREMENT IN SURFACE WATER

When using a single-parameter pH electrode/meter instrument system, the pH of surface water is determined ex situ, from a quiescent, non-stirred sample that is withdrawn from a churn or cone splitter or other approved sample-compositing device. Although referred to as a single-parameter method, most modern pH meters are equipped with a thermistor used to determine the temperature of the sample. Each pH measurement must be accompanied with a concurrent temperature measurement.

▶ It is not advisable to immerse the pH electrode into flowing surface water for the following reasons:

    — Placing the pH electrode into moving water risks damage to the delicate glass membrane (scratching, pitting, coating), which will inhibit the correct functioning of the electrode. In addition, proper functioning of the glass membrane is affected when ionic equilibrium is not achieved with the surrounding sample solution.

    — Calibration of the electrode was accomplished in a quiescent sample, not in flowing or stirred water. Adequate calibration of the instrument system cannot be assumed to extend to moving water.

    — USGS methodology in surface-water measurement usually involves the collection of depth- and width-integrated samples. In situ measurements of pH in a moving water system, either at a singular point in the waterway or across a section, do not meet these requirements.

    — Reference-junction equilibrium cannot be achieved in moving water; thus, correct electrode functioning will again be inhibited.

    — It is difficult to have electrode temperature come to equilibrium with sample temperature in moving water; correct pH instrument system functioning will be inhibited.

▶ The determination of pH in situ, using a multiparameter instrument system, is described in NFM 6.0 and 6.8. The system selected depends on the data-quality objectives of the study and on site-specific conditions.

Before collecting the sample and making ex situ measurements, it is advisable to determine the range of pH values in the cross section, or estimate the magnitude of lateral mixing of the waterway at the field site, using an in situ measurement method (for example, with a multiparameter sonde).

When making an ex situ pH measurement:

Set up the pH instrument system close to the sampling site in order to minimize the time lapse between sample collection and pH measurement.

1. The glass membrane of the electrode should not contact the sides or bottom of the beaker or other measurement vessel. Use only a clean measurement vessel.

2. Fill the measurement vessel with sufficient sample to ensure that the electrode reference junction is fully immersed, taking care not to aerate the sample.

3. After calibration (or measuring the pH of a different sample), rinse the electrode and thermistor three times with DIW. This crucial step must always be completed between differing solutions.

4. **Rinse the electrode and thermistor sensors two times with the sample**, as follows:

    a. **First rinse—**Pour an aliquot of sample onto the sensors and swirl the sample water around the electrode sensors. Discard the sample appropriately.

    b. **Second rinse—**Pour an aliquot of sample onto the sensors and allow the sensors to sit in the solution for 1 minute (do not swirl). Discard the sample appropriately.

5. **Measure pH**, as follows:

    a. Pour a third aliquot of sample into the vessel. **Allow the sensors to sit in a quiescent sample** for 1 minute or until the pH value stabilizes within the established criterion. Record the pH value on the electronic or paper field-notes form.

    b. Repeat the procedure in (a) above on at least two additional aliquots of the sample, recording the pH measurement for each aliquot on the field form(s).

6. **Calculate a final sample pH as the median** of the values measured for the sample aliquots and document the calculation on field forms.

7. **Record** the final pH value of the sample to the nearest 0.01 pH unit, along with the sample temperature, in paper and (or) electronic field forms, including forms that accompany samples being shipped to the laboratory.

8. The pH value should be reported to the nearest 0.1 pH unit when published and when recorded in the NWIS database.

> **Always record the temperature of the sample concurrently with each pH measurement.**

6.4.4.B   pH MEASUREMENT IN GROUND WATER

The pH of ground water should be measured under no-flow (quiescent sample) conditions. When using a single-parameter meter, the measurement can be made either with the pH electrode and temperature sensor inserted (a) into an airtight flowthrough cell or chamber to which the sample is pumped, or (b) in a vessel that contains an aliquot of sample either collected from pump discharge or withdrawn from a sampling device, such as a bailer (figs. 6.4–2 and 6.4–3, respectively). (See NFM 6.8 for pH measurement using a multiparameter sonde).

The central concept for measuring pH in ground water is to use equipment that minimizes aeration, chemical change, and temperature change. If possible, operate equipment in a manner that helps to mitigate losses and gains of dissolved gases in solution.
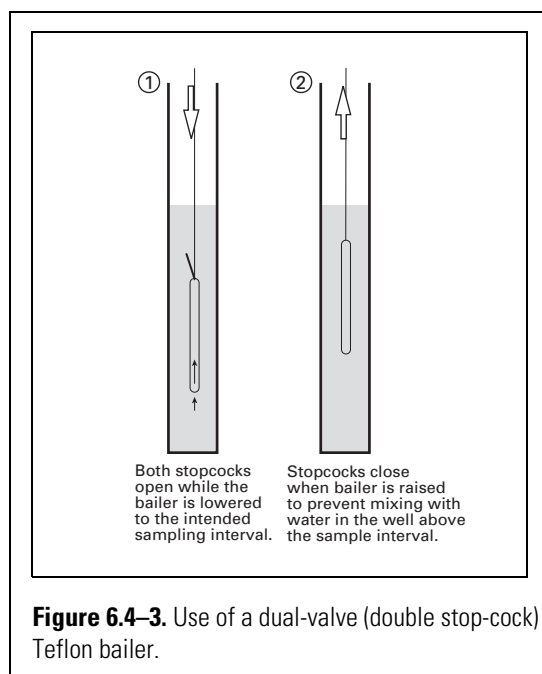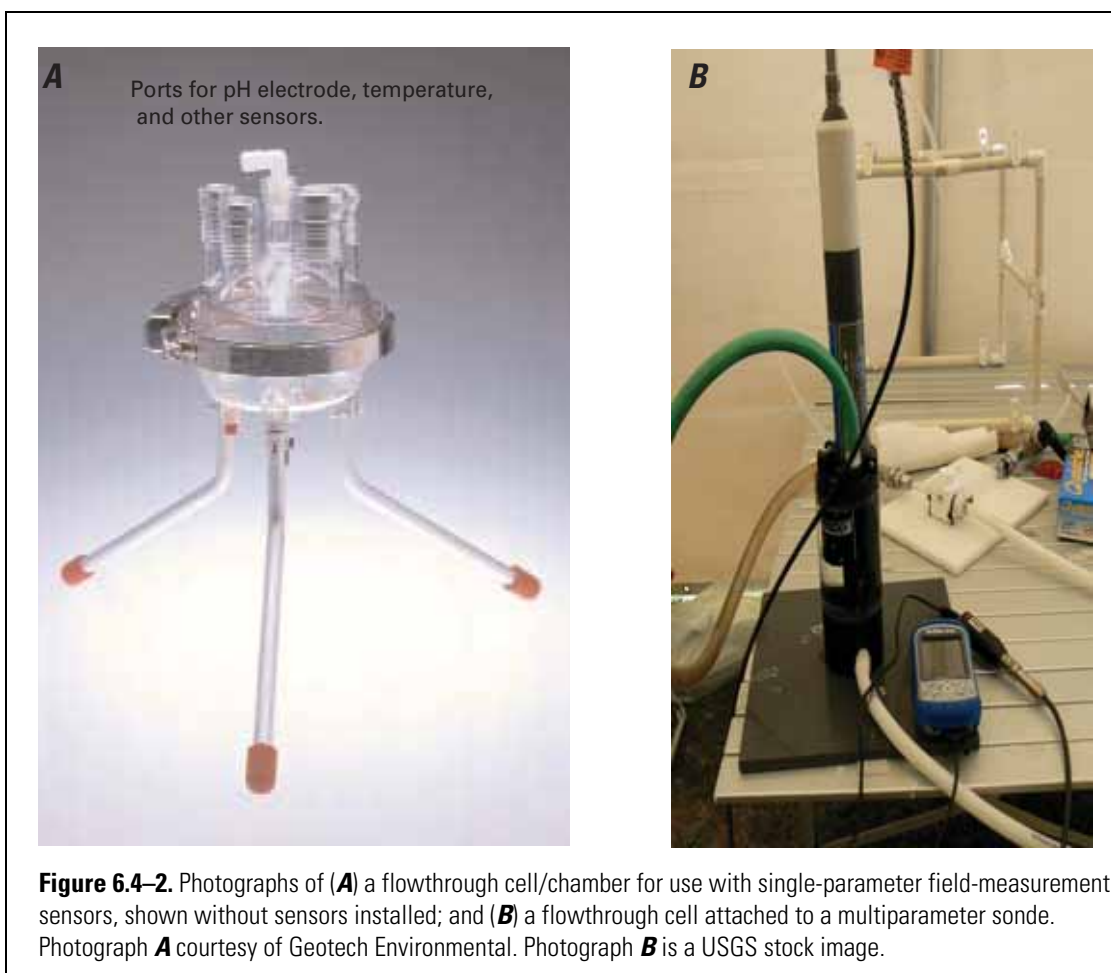
▶   The flowthrough cell/chamber method yields accurate pH data when implemented appropriately.

▶   Bailed or other methods for collecting discrete samples for pH measurement must be implemented carefully to avoid temperature change, turbulence, and sample aeration from decanting and mixing of the bailed water.

▶   Downhole deployment of a submersible sensor or sonde risks losing the equipment if it becomes lodged in the well.

> **Document on electronic or paper field forms the methodology used to obtain samples for pH measurement.**

Unless specifically required by study objectives or environmental constraints, in situ measurement of pH by putting the sensor system directly into the well (downhole method) should be avoided for the following reasons:

▶   Placing the pH electrode directly into the borehole risks damage to the delicate glass membrane (scratching, pitting, coating), which will inhibit the correct functioning of the electrode. Any accretions or coatings on the inside of the borehole may be transferred to the pH sensor and damage, or alter, the membrane.

▶   Pumps, wiring, and (or) other equipment within the borehole may damage or degrade the pH sensor and the sonde.

▶   Any static electrical charge on the inside of the well casing or borehole may be transferred to the pH electrode, a condition sometimes referred to as a "ground loop," which also compromises accurate pH measurement.

> **Always measure and record sample temperature concurrently with pH measurements.**

Figure 6.4–2. Photographs of (***A***) a flowthrough cell/chamber for use with single-parameter field-measurement sensors, shown without sensors installed; and (***B***) a flowthrough cell attached to a multiparameter sonde. Photograph ***A*** courtesy of Geotech Environmental. Photograph ***B*** is a USGS stock image.

Figure 6.4–3. Use of a dual-valve (double stop-cock) Teflon bailer.

Referring to figure 6.4–2, ground water is pumped directly from the well through tubing and into an airtight flowthrough cell/chamber containing either a calibrated pH electrode and other sensors (typically, dissolved oxygen, specific electrical conductance, and temperature sensors (fig. 6.4–2A), or a multiparameter sonde (fig. 6.4–2B).

After successful calibration of the pH instrument system on site, pH measurement of sample water may proceed either on discrete samples obtained from a bailer, or on pumped ground water circulated through a flowthrough cell/chamber.

▶ Use of the bailer to obtain ground-water samples is analogous to the approved use of samplers in a surface-water situation, as described below.

▶ Use of a flowthrough cell/chamber has the advantage of concurrent monitoring of ground-water field measurements in addition to pH, as described below.

To make a pH measurement using a flowthrough cell/chamber system instrumented with single-parameter sensors (fig. 6.4–2):

1. Install the chamber system as close to the well as possible and shield the chamber and tubing from direct sunlight.

2. Check that the electrode fill hole is open to the atmosphere and that the reference junction is entirely submerged.

3. Check for and eliminate any backpressure condition.

4. Monitor pH variation during purging:

    a. Keep the flow constant and laminar.

    b. Allow the sensors to equilibrate with the ground water for 5 minutes or more, at the flow rate to be used for collecting all of the other samples.

    c. Record pH values at regularly spaced time intervals throughout purging (consult NFM 6.0 for detailed guidance). Compare the variability of pH values toward the end of purging. The stability of pH values is assumed when three to five readings made at regularly spaced intervals are constant. If readings continue to fluctuate, continue to monitor, or, if site conditions are demonstrably variable (degassing, in-gassing, rapid thermal changes from water at depth), select the median of three or more readings within about 60 seconds as the value recorded for the specific time interval.

5. Determine sample pH toward the end of purging (for example, during removal of the final purge volume) as follows:

    a. Divert flow from the chamber to allow the sample contained within the chamber to become quiescent (after recording the other field measurements). Record the pH value under quiescent conditions to the nearest 0.01 pH unit.

    b. Determine the median of the pH values recorded under quiescent conditions and report this value as sample pH.

    c. If field personnel have reason to suspect an electrode malfunction, a calibration check at the end of sampling is recommended.

To make a pH measurement on a bailed sample (fig. 6.4–3):

1. Withdraw subsamples from the well and transfer each bailed sample to a churn, cone splitter, or other appropriate compositing device (NFM 2).

2. Remove an aliquot from the sample composite for measurement of pH.

TROUBLESHOOTING 6.4.5

Consult the instrument manufacturer for recommended troubleshooting actions for specific single-parameter and multiparameter pH instrument systems.

▶ Nearly all problems encountered during pH calibration and measurement can be attributed directly to the condition and responsiveness of the pH electrode (table 6.4–3).

▶ For any problem, first test that the instrument batteries are fully charged. Keep spare batteries on hand that are fully charged.

Table 6.4–3. Troubleshooting guide for pH measurement.

[DIW, deionized water]

Symptom	Possible cause—Corrective action
Instrument system will not calibrate to full scale	• Buffers may be contaminated or old—Use fresh buffers. • Faulty electrode—Recondition or replace electrode (see section 6.4.2). • Weak batteries—Replace with new or fully charged batteries.
Slow response	*For liquid-filled electrodes:* • Weak or incorrect solution—Change filling solution to correct molarity. • No or low filling solution—Add fresh solution of correct molarity. • Dirty tip (for example, visible chemical deposits or organic or biological matter on the electrode)—Rinse tip with DIW; if residue persists, use solution and cleaning method recommended by the manufacturer. **Take care not to scratch the electrode tip.** • Clogged or partially clogged junction—Follow the manufacturer's instructions to unclog the junction). • Water is cold or of low ionic strength—Allow more time for equilibration; consider using a different electrode (section 6.4.3.B). • Sluggish response to pH changes; pH measurement is biased negatively—Refer to table 6.4–2. *For gel-filled electrodes:* • Dirty bulb—Rinse bulb carefully with DIW. If organic/inorganic/biological residue persists, consult the manufacturer's recommendations. • Visibly clogged junction—Follow the manufacturer's instructions to unclog the junction • Water is cold or of low ionic strength—Allow more time for equilibration; consider using a different electrode (section 6.4.3.B).
Erratic readings	• Loose or defective connections—Tighten, clean, or replace connections. • Broken or defective cable—Repair or replace cable. • Static charge—Polish face of meter with antistatic solution. • Loose battery connection—Tighten. • Air bubbles in the electrode bulb—Shake electrode gently. • Too much pressure in flowthrough chamber—Release and reduce pressure. • Weak batteries—Replace with new, fully charged batteries.

6.4.6   REPORTING

Due to the rapidity of pH reactions in environmental samples, the effect of temperature on the operation of the pH instrument system, and chemical and microbiological equilibria within the sample, pH measurements must be completed and recorded as soon as possible after removing the sample from the environmental medium. When entering the pH value for the site into the NWIS database, ensure that the method code selected correctly corresponds to the method that was used for the pH measurement.

▶   On field forms (electronic or paper) and in the pH-meter/electrode logbook, record pH calibration and environmental measurements to 0.01 standard pH units.

▶   In the USGS NWIS database, report pH values to the nearest 0.1 standard pH unit, unless study and data-quality objectives dictate otherwise and equipment of the appropriate precision and accuracy has been used.

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6.4.8 ACKNOWLEDGMENTS